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THEREOF IN WATER TREATMENT TO CONTROL MICROBIAL FOULING

(57) Abstract

The invention is a method for preparing a stabilized aqueous alkali or alkaline earth metal hypobromite solution. The method comprises the steps of: a) mixing an aqueous solution of alkali or alkaline earth metal hypochlorite having from about 5 percent to about 70 percent available halogen as chlorine with a water soluble bromide ion source; b) allowing the bromide ion source and the alkali or alkaline earth metal hypochlorite to react to form a 0.5 to 70 percent by weight aqueous solution of unstabilized alkali or alkaline earth metal hypobromite; c) adding to the unstabilized solution of alkali or alkaline earth metal hypobromite an aqueous solution of an alkali metal sulfamate in a quantity to provide a molar ratio of alkali metal sulfamate to alkali or alkaline earth metal hypobromite is from about 0.5 to about 7; and, d) recovering a stabilized aqueous alkali or alkaline earth metal hypobromite solution.

**A PROCESS TO MANUFACTURE STABILIZED ALKALI OR ALKALINE
EARTH METAL HYPOBROMITE AND USES THEREOF IN WATER
TREATMENT TO CONTROL MICROBIAL FOULING**

The present invention relates to a method of preparing a stabilized alkali or alkaline earth metal hypobromite to control microbiofouling, more specifically, a stabilized sodium hypobromite solution the characteristics of which include non-volatility, high free halogen residual, lower bromate formation, reduced generation of absorbable organic halogen in process waters, as well as improved performance against biofouling.

Background of the Invention

Aqueous solutions of sodium hypochlorite are widely used in cooling water towers; bleaching processes; treatment of recreational waters including swimming pool water, water slide and other water game equipment, spas, and whirlpools; disinfectants; laundry detergents; and, industrial biocides including applications in the petroleum industry. However, a major disadvantage of NaOCl is its instability. As is well known in the art, several methods are used to stabilize NaOCl. The Self et al. reference (U.S. Pat. No. 3,328,294) described a continuous process to stabilize hypochlorite with an equal molar ratio of sulfamic acid. This process was improved upon by Rutkiewicz reference (U.S. Pat. No. 3,767,586) who added a buffer which aided in pH control increasing the stability of concentrated solutions.

Bromine has various advantages over chlorine for water treatment such as better performance in high pH or amine environments and a lower volatility.

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provide a stable bromine product that can be safely and easily handled while meeting environmental requirements (more fully discussed below), such as low bromate and absorbable organic halogen generation, and having a high free halogen residual and a low volatility (resulting in a greatly reduced odor and vapor-phase corrosion). In addition, a portion of the expensive bromine compound is wasted through an ineffective by-product in some delivery schemes. Thus, the need for a safe, convenient, economical, stable bromine water treatment product remains and is significant.

The Goodenough et al. reference (U.S. Pat. No. 3,558,503), teaches stabilization of bromine using any compound which reacted reversibly with bromine. The disclosed compounds include:

- (a) water-soluble primary and secondary amines or amides; and,
- (b) sulfamic acid and its water-soluble salts.

However, the bromine solutions prepared according to the Goodenough et al. reference teachings are not stable enough for practical use in commercial cooling water, oil field and other industrial applications.

Sulfamic acid, according to the Goodenough et al. reference, is employed as a free acid or as one of its water-soluble salts such as the sodium, potassium or ammonium salt. However, the manner in which the bromine solutions are prepared provide relatively low stabilities and low available halogen concentrations compared with the discoveries claimed within this invention disclosure. The Goodenough et al.

The method described in the Goodenough et al. reference could not achieve these increased bromine levels as the order of reagent addition described in the reference was deemed not critical to the operability of the method. Since NaOBr is synthesized by the following reaction, $\text{NaOCl} + \text{NaBr} \rightarrow \text{NaOBr} + \text{NaCl}$, addition of the stabilizer prior to bromide oxidation would not permit the formation of NaOBr.

When water is treated with many halogenated biocides, undesirable halogenated organics can be generated as by-products. These compounds are causing increased environmental and health concerns. It is generally known that low molecular weight halogenated organics are more easily biologically degraded than higher molecular weight species. However, the low molecular weight forms may be more toxic to aquatic and mammalian organisms. Differentiation of these halogenated organics is costly, time consuming and requires the use of gas chromatography, high performance liquid chromatography or gel permeation chromatography. Absorbable Organic Halogen, "AOX", was chosen as a method of measuring the sum of halogenated organic compounds without speciation. AOX is used as an effluent monitoring parameter of water or wastewater in Europe and North America. In the United States, the Environmental Protection Agency ("EPA") is looking closely at AOX discharge in the pulp and paper industry. An object of the present invention is to provide a stable NaOBr solution that can be used to control microbial fouling with minimal AOX generation. The problems associated with controlling AOX levels,

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Another object of the present invention is to provide a stable sodium hypobromite solution in which the formation of AOX is minimized while providing improved microbial fouling control. Other objects and advantages of the present invention will become obvious from the following description thereof.

Summary of the Invention

The invention, according to one embodiment is a method for preparing a stabilized aqueous alkali or alkaline earth metal hypobromite solution. The method comprises the steps of:

- a. Mixing an aqueous solution of alkali or alkaline earth metal hypochlorite having from about 5 percent to about 70 percent available halogen as chlorine with a water soluble bromide ion source;
- b. Allowing the bromide ion source and the alkali or alkaline earth metal hypochlorite to react to form a 0.5 to 70 percent by weight aqueous solution of unstabilized alkali or alkaline earth metal hypobromite;
- c. Adding to the unstabilized solution of alkali or alkaline earth metal hypobromite an aqueous solution of an alkali metal sulfamate in a quantity to provide a molar ratio of alkali metal sulfamate to alkali or alkaline earth metal hypobromite is from about 0.5 to about 7; and,
- d. Recovering a stabilized aqueous alkali or alkaline earth metal hypobromite solution.

Description of the Preferred Embodiments

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the examples, in a more preferred embodiment, the alkali or alkaline earth metal hypochlorite is sodium hypochlorite, the bromide ion source is sodium bromide, and the alkali or alkaline earth metal hypobromite is sodium hypobromite.

The aqueous solution of unstabilized alkali or alkaline earth metal hypobromite may contain from about 0.5 to about 70 percent by weight alkali or alkaline earth metal hypobromite, more preferably from about 1 to about 30 percent by weight alkali or alkaline earth metal hypobromite, and most preferably from about 4 to about 15 percent by weight alkali or alkaline earth metal hypobromite.

The pH of the stabilized aqueous alkali or alkaline earth metal hypobromite solution is from about 8 to about 14 and more preferably from about 11 to about 14. The the molar ratio of the alkali metal sulfamate to the sodium hypobromite is preferably from about 0.5 to about 7, more preferably from about 0.5 to about 4, and most preferably from about 0.5 to about 2.

Another embodiment of the invention is a stabilized aqueous solution of an alkali or alkaline earth metal hypobromite which is prepared by the steps of:

- a. Mixing an aqueous solution of alkali or alkaline earth metal hypochlorite having from about 5 percent to about 70 percent available halogen as chlorine with a water soluble bromide ion source;
- b. Allowing the bromide ion source and the alkali or alkaline earth metal hypochlorite to react to form a 0.5 to 30 percent by weight aqueous solution of unstabilized alkali or alkaline earth metal hypobromite;

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The pH of the stabilized aqueous alkali or alkaline earth metal hypobromite solution is from about 8 to about 14 and more preferably from about 11 to about 14. The the molar ratio of the alkali metal sulfamate to the sodium hypobromite is preferably from about 0.5 to about 7, more preferably from about 0.5 to about 4, and most preferably from about 0.5 to about 2.

The invention can be used in an industrial water system. Such water systems would contain from about 0.05 to about 1000 ppm, more preferably from about 0.05 to about 10 ppm, and most preferably from about 0.1 to about 5 ppm of the stabilized aqueous solution of an alkali or alkaline earth metal hypobromite.

The invention can be used in the laundering of soiled garments where the soiled garments are washed in an aqueous media, such as water, containing a detergent and a bleaching agent. The stabilized aqueous solution of an alkali or alkaline earth metal hypobromite can be used as the bleaching agent.

The invention can also be used in the manufacture of cellulosic materials in which cellulosic fibers are bleached with an oxidizing agent. The stabilized aqueous solution of an alkali or alkaline earth metal hypobromite can be used as the oxidizing agent.

The invention can be used in the control of microbiofouling in a recreational water system in which an oxidizing agent is added to control microbiofouling. The stabilized aqueous solution of an alkali or alkaline earth metal hypobromite can be used as the oxidizing agent.

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The industrial water systems include cooling water systems, cooling ponds, reservoirs, sweetwater applications, decorative fountains, pasteurizers, evaporative condensers, hydrostatic sterilizers and retorts, gas scrubber systems, and air washer systems.

Another embodiment of the invention is a method for preparing a stabilized aqueous alkali or alkaline earth metal hypobromite solution when the level of available halogen as chlorine is below about 5 percent. The method comprises the steps of:

- a. Mixing an aqueous solution of alkali or alkaline earth metal hypochlorite [wherein the percent of available halogen (as chlorine) is less than about 5] with a water soluble bromide ion source;
- b. Allowing the bromide ion source and the alkali or alkaline earth metal hypochlorite to react to form a 0.5 to 5 percent by weight aqueous solution of unstabilized alkali or alkaline earth metal hypobromite;
- c. Adding to the unstabilized solution of alkali or alkaline earth metal hypobromite an aqueous solution of an alkali metal sulfamate having a temperature of at least 50 °C in a quantity to provide a molar ratio of alkali metal sulfamate to alkali or alkaline earth metal hypobromite is from about 0.5 to about 7; and,
- d. Recovering a stabilized aqueous alkali or alkaline earth metal hypobromite solution.

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alkali or alkaline earth metal hypobromite, and most preferably from about 4 to about 15 percent by weight alkali or alkaline earth metal hypobromite.

The pH of the stabilized aqueous alkali or alkaline earth metal hypobromite solution is from about 8 to about 14 and more preferably from about 11 to about 14.

The the molar ratio of the alkali metal sulfamate to the sodium hypobromite is preferably from about 0.5 to about 7, more preferably from about 0.5 to about 4, and most preferably from about 0.5 to about 2.

Another embodiment of the invention is a stabilized aqueous solution of an alkali or alkaline earth metal hypobromite which is prepared by the steps of:

- a. Mixing an aqueous solution of alkali or alkaline earth metal hypochlorite [wherein the percent of available halogen (as chlorine) is less than about 5] with a water soluble bromide ion source;
- b. Allowing the bromide ion source and the alkali or alkaline earth metal hypochlorite to react to form a 0.5 to 5 percent by weight aqueous solution of unstabilized alkali or alkaline earth metal hypobromite;
- c. Adding to the unstabilized solution of alkali or alkaline earth metal hypobromite an aqueous solution of an alkali metal sulfamate having a temperature of at least 50 °C in a quantity to provide a molar ratio of alkali metal sulfamate to alkali or alkaline earth metal hypobromite is from about 0.5 to about 7; and,
- d. Recovering a stabilized aqueous alkali or alkaline earth metal hypobromite solution.

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metal hypobromite, more preferably from about 1 to about 30 percent by weight alkali or alkaline earth metal hypobromite, and most preferably from about 4 to about 15 percent by weight alkali or alkaline earth metal hypobromite.

The pH of the stabilized aqueous alkali or alkaline earth metal hypobromite solution is from about 8 to about 14 and more preferably from about 11 to about 14.

The the molar ratio of the alkali metal sulfamate to the sodium hypobromite is preferably from about 0.5 to about 7, more preferably from about 0.5 to about 4, and most preferably from about 0.5 to about 2.

In another embodiment, the invention is a method of preventing microbiofouling on the surfaces of equipment in contact with in an industrial water system. The method comprises adding to the aqueous system an anti-microbiologically effective amount of a stabilized sodium hypobromite solution. The stabilized sodium hypobromite solution is prepared by the steps of:

- a. Mixing an aqueous solution of sodium hypochlorite [wherein the percent of available halogen (as chlorine) is less than about 5] with sodium bromide;
- b. Allowing the sodium bromide and the sodium hypochlorite to react to form a 0.5 to 5 percent by weight aqueous solution of unstabilized sodium hypobromite;
- c. Adding to the unstabilized solution of sodium hypobromite an aqueous solution of an alkali metal sulfamate having a temperature of at least 50 °C in a

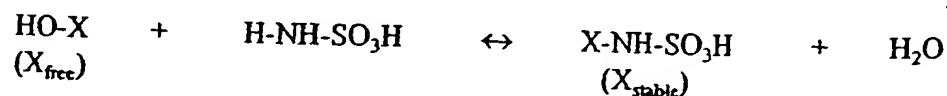
H or NH₂ group adjacent to an electron withdrawing functional group such as C=O, S=O, P=O, or B=O.

This invention provides several differences over the known art, including a specific order of addition in the manufacturing process whereby a stabilized sodium hypobromite solution is produced having improved stability, non-volatility, reduced bromate and AOX formation, improved microfouling control, and an increased free halogen residual in cooling water.

The stability of the stabilized hypobromite solution, as compared to the stabilized bromine disclosed in the Goodenough et al. reference and unstabilized sodium hypobromite in Table I, is greatly increased. Based on the surprising increased stability of the stabilized sodium hypobromite of this invention, it is apparent that the order of addition in the process of manufacture is critical.

TABLE I					
INCREASED STABILITY OVER PRIOR ART % LOSS OF AVAILABLE HALOGEN					
	After 4 days	After 14 days	After 21 days	After 34 days	After 84 days
Goodenough et al.	21	23	--	--	--
Stabilized Sodium Hypobromite	0	0	0	1	1
Unstabilized Sodium Hypobromite	--	74	79	84	93

The chemical mechanism for halogen biocide stabilization by sulfamic acid has been proposed as follows:



When X is Cl, the reaction applies to stabilized chlorine.

When stabilized chlorine is used as a biocide, only Pathway B is possible because no free HOCl exists in the system. Thus, no or very low AOX will be formed using this product (see Table II below).

When stabilized bromine is used, both free and stabilized bromine forms coexist. Thus, both pathways A and B proceed and result in some AOX formation. However, the amount of AOX will be far less than when all of the halogen is in the form of free bromine (HOBr).

Apparently, the proposed mechanism explains the cause of AOX reduction due to the use of stabilized halogen biocides. The mechanism should be applicable to other stabilized halogen products when ammonia, amines or amides are used as the stabilizing agents.

In order to reduce the AOX formation by a stabilized halogen biocide, it is preferable to select strong stabilizing agents so that Pathway B can dominate. However, the drawback to a very stable halogenated compound is the generally decreased oxidation power that, in most cases, is directly correlated to its biocidal efficacy. Testing has shown that stabilized bromine is much more effective as a biocide than stabilized chlorine. Therefore, to reduce the AOX formation and at the same time maintain the compound's biocidal efficacy requires a well balanced selection of the stabilizing agent.

the prior art as the decline of active ingredient was only 1 percent after 84 days (see Table I above). An unstabilized NaOBr solution prepared in an similar process by replacing sulfamic acid with distilled water lost 94 percent available halogen during the same period.

Example 2:

Less AOX is Formed in Stabilized Halogen Solutions

AOX is a generic class of compounds which includes all organic molecules containing halogen. Limits for AOX discharge from cooling water systems have already been established in some European countries. To simulate AOX formation during stabilized and unstabilized sodium hypobromite action in cooling water, a mixed bacterial culture typically found in cooling water was cultivated in L-broth overnight and the cells harvested by centrifugation. The cell pellet was washed with synthetic cooling water (90 ppm calcium, 50 ppm magnesium, 110 ppm "M" alkalinity, pH 8.0 -8.2) twice to remove the remaining organic medium. Cells were then resuspended into an equal volume of cooling water. A capped dark bottle served as the reactor. Synthetic cooling water was added to the bottle followed by the washed bacterial stock yielding approximately 10^7 cells/ml. Stabilized NaOBr or unstabilized NaOBr was dosed into this bacterial suspension at a final concentration of 1, 2, 3, or 4 ppm total halogen (as chlorine). Headspace in the bottle was minimized to avoid the evaporative loss of halogenated organics and the solution stirred for 24 hours to simulate a typical cooling system. Immediately before AOX analysis, the

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Freshly prepared solutions of stabilized and unstabilized sodium hypobromite were diluted then added to cooling water in order to achieve a one ppm free halogen residual (as chlorine). Sodium hypochlorite was stabilized in the same fashion as described for NaOBr in Example One with the exception that NaBr was directly replaced with distilled water. Stabilized and unstabilized sodium hypochlorite were diluted then added to cooling water at a final concentration of one ppm free halogen residual (as chlorine). The volumes of all solutions needed to achieve a one ppm free halogen residual (as chlorine) was recorded. Following 6 and 21 days of dark storage, identical dilutions of stabilized and unstabilized sodium hypochlorite solutions were prepared and the volume originally required for a one ppm free halogen residual (as chlorine) was added to cooling water containing approximately 10^6 *Pseudomonas aeruginosa* cells / mL. Aliquots were extracted at 10 and 30 minutes into cooling water dilution blanks containing a halogen neutralizer (0.05 percent $\text{Na}_2\text{S}_2\text{O}_3$) then enumerated on tryptone glucose extract agar. Stabilized NaOBr retained its antibacterial activity after storage while the unstabilized form lost its efficacy against *Pseudomonas aeruginosa* (see Table III below). The results were even more dramatic as the storage period increased. This effect was likely due to the disproportionation of the unstable hypobromite ion into the non-biocidal species bromide and bromate. Surprisingly, NaOCl stabilized in the same manner as NaOBr was comparatively ineffective under the conditions tested (Table III).

condition suitable for bromate formation, were assayed for bromate. A Dionex 4000 series gradient ion chromatography system equipped with AG9-SC/AS9-SC columns and a conductivity detector was used to measure the bromate concentration in the samples. The chromatograph was operated according to a method currently under investigation by the EPA for the analysis of bromate in ozonated drinking water. Purified water from an Interlake Water Systems deionization system was used for the preparation of all reagents and standard solutions to prevent contamination.

TABLE IV		
BROMATE FORMATION IN STABILIZED & UNSTABILIZED NaOBr SOLUTIONS STORED FOR EIGHT MONTHS		
PERCENT BROMATE	STABILIZED NaOBr	UNSTABILIZED NaOBr
	0.004	2.700

As noted above, the pH of these solutions was high which favors bromate formation. However, NaOCl, which contains significant amounts of NaOH, is typically diluted with system water prior to the introduction of the bromide species in most industrial applications. The pH of this diluted system would be lower than the neat NaOCl / NaBr formulation described above theoretically minimizing bromate formation. The available chlorine in a NaOCl sample diluted (1:100) with distilled water was titrated by the DPD-FAS method. A solution of 45 percent sodium bromide was added to the dilute NaOCl at a molar ratio of $1 \text{ Cl}_2 : 1 \text{ Br}^-$ forming NaOBr. This reaction proceeded for thirty minutes. Then, appropriate volumes of this dilute NaOBr solution were added to cooling water (pH 8.3) giving total available halogen levels of

when employing stabilized NaOBr. A commercial heating, ventilation and air conditioning ("HVAC") cooling system was sequentially treated with stabilized NaOCl, a bromochloroalkylhydantoin, and finally stabilized NaOBr. There was a low percentage of free chlorine relative to total available halogen present in the stabilized NaOCl treated system (see Table V below). A lower percentage of free halogen was measured when a different stabilization system, an alkylhydantoin, was employed with bromine and chlorine (see Table V below). However, when stabilized NaOBr was fed into this system, the percentage of free available halogen relative to the total residual measured quickly increased (see Table V below). These phenomena imply that less stabilized NaOBr is required to obtain a free available halogen residual than the equivalent amount of stabilized NaOCl.

TABLE V		
FREE RESIDUAL OXIDANT AS A PERCENT OF TOTAL RESIDUAL OXIDANT IN RECIRCULATING COOLING WATER SYSTEM		
Days in System	Average Free Oxidant as a Percent of Total Residual Oxidant	Biocide Employed
36	13	stabilized NaOCl
45	9	halogenated hydantoins
33	53	stabilized NaOBr

Example Six:

Stabilization of Sodium Hypobromite Reduces Volatility

If a biocide is highly volatile, its performance may be adversely affected. For example, the biocide may flash off in the highly aerated conditions of a cooling tower or an air washer. This would lower the biocide concentration in the cooling water

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were encountered in either the air washer unit or the return air. The microbial population was enumerated before and after stabilized NaOBr addition. The microbial population following dosing was reduced by greater than one order of magnitude. This example demonstrates the utility of stabilized sodium hypobromite in controlling the bacterial population while adding no halogen odor to the system area.

Changes can be made in the composition, operation and arrangement of the method of the present invention described herein without departing from the concept and scope of the invention as defined in the following claims:

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consisting of urea, thiourea, creatinine, cyanuric acids, alkyl hydantoins, mono or di ethanolamine, organic sulfonamides, biuret, sulfamic acid, organic sulfamates and melamine.

4. A stabilized aqueous solution of an alkali or alkaline earth metal hypobromite which is prepared by the steps of:

- a. Mixing an aqueous solution of alkali or alkaline earth metal hypochlorite having from about 5 percent to about 70 percent available halogen as chlorine with a water soluble bromide ion source;
- b. Allowing the bromide ion source and the alkali or alkaline earth metal hypochlorite to react to form a 0.5 to 30 percent by weight aqueous solution of unstabilized alkali or alkaline earth metal hypobromite;
- c. Adding to the unstabilized solution of alkali or alkaline earth metal hypobromite a stabilizer selected from the group consisting of carbonic acids, hydrogen cyanide, carboxylic acids, amino acids, sulfuric acids, phosphoric acids and boric acids;
- d. Recovering a stabilized aqueous alkali or alkaline earth metal hypobromite solution.

5. The method of claim 4, wherein the stabilizer is selected from the group consisting of urea, thiourea, creatinine, cyanuric acids, alkyl hydantoins, mono or di ethanolamine, organic sulfonamides, biuret, sulfamic acid, organic sulfamates and melamine.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C01B C02F C11D 021C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	WO 97 34827 A (NALCO CHEMICAL CO) 25 September 1997 see the whole document	1-7
X	US 4 992 209 A (SMYK EUGENE B ET AL) 12 February 1991 see example 2	1, 4-7
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A	US 5 641 520 A (HOWARTH JONATHAN N ET AL) 24 June 1997 see claims	1-7
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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